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THERMAL DECOMPOSITION OF HEXAMMINECHROMIUM (III) CHLORIDE

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In this paper the results of comparative thermal analysis TG-DTG-DTA-DSC for the thermal decomposition process of $[Cr(NH_3)_6]Cl_3$ in air atmosphere are given. The kinetics and mechanism of this complex thermal decomposition, process enthalpy as the changes of specific thermal capacity of solid products reaction with temperature were determined.

Numerous authors were studied thermal stability of hexamminechromium(III)chloride [1-3]. The deamination reaction for $[Cr(en)_3]Cl_3$ occurs at 260° although the similar complex with ethulamine is less stable no DTA curve is known to the author [1]. It is interesting to note that $[Cr(NH_3)_6]Cl_3$ is just as stable as $[Cr(en)_3]Cl_3$. The initial reaction, however, is more severe in the decomposition of the amine complex, which loses three molecules of NH_3 to give $[Cr(NH_3)_3]c_{13}$ at 280° whereas the ethylenediamine complex loses only one molecule of ethylenediamine [2-3]. The electric features of this type chrome compound were studied by Grotovska and Wojcichowski [4].

In this paper is given a contribution to the comparative study of thermal decomposition process of hexamminechromium(III)chloride by use of DTA-TG-DTG simultaneous analysis as well as by use of DSC measurements of process enthalpy and C_p change (specific thermal capacity) of solid products reaction, developed during thermal decomposition process.

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Experimental

In this paper are presented the analyzing results of $[Cr(NH_3)_6]Cl_3$ sample, whose characteristics were published earlier [5-6]. Thermal analysis results were carried out on Derivatograph 1500, manufactured by MOM Company from Budapest, Hungary, and DSC analysis were carried out on DSC-404 apparatus, manufactured by NETZSCH Company. All analysis were carried out in air atmosphere.

Results and discussion

The results of simultaneous DTA-TG-DTG analysis for $[Cr(NH_3)_6]Cl_3$ in air atmosphere at heating rate of 10° deg/min are shown in Fig. 1. Based on the results of TG and DTG measurements, with error less than 5%, it was determined the following process mechanism:

$$[Cr(NH_3)_6]Cl_3 \rightarrow [Cr(NH_3)_2]Cl_3 + 4NH_3 \tag{1}$$

$$[Cr(NH_3)_2]Cl_3 \rightarrow CrCl_3 + 2\,NH_3 \tag{2}$$

$$2CrCl_3 + 1.5O_2 \rightarrow Cr_2O_3 + 3Cl_2 \tag{3}$$

Based on the results from Fig. 1 using of TG data for mass sample loss during heating, by Freeman and Carroll [7], it was determined the kinetics parameters: activation energy (E) and reaction order (n) for (1); (2) and (3) processes, which are developed during thermal decomposition of hexamminechromium(III) chloride. Resulting dependence from Freeman and Carroll [7] method:

$$\frac{\frac{E}{2.3R}\Delta\left(\frac{1}{T}\right)}{\Delta\log m_r} = -n + \frac{\Delta\log \mathrm{d}m/\mathrm{d}t}{\Delta\log m_r} \tag{4}$$

for processes in thermal decomposition of hexamminechromium(III) chloride, is shown in Fig. 2. Signs in Eq. (4) have the following meaning: E-activation energy; n-reaction order, R-universal gas constant; T-absolute temperature and m_r-total mass loss.

Based on the results, shown in Fig. 2, the following values for activation energy are determined: 54; 20 and 11 kJ/mol for (1), (2) and (3) processes,

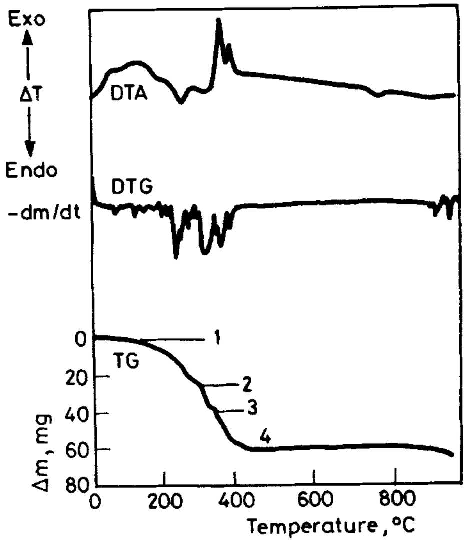

Fig. 1 The results of simultaneous DTA-TG-DTG analysis for $[Cr(NH_3)_6]Cl_3$ in air atmosphere at heating rate of 10°/min. 1 - $[Cr(NH_3)_6]Cl_3$; 2 - $[Cr(NH_3)_2]Cl_3$; 3 - $CrCl_3$; 4 - Cr_2O_3

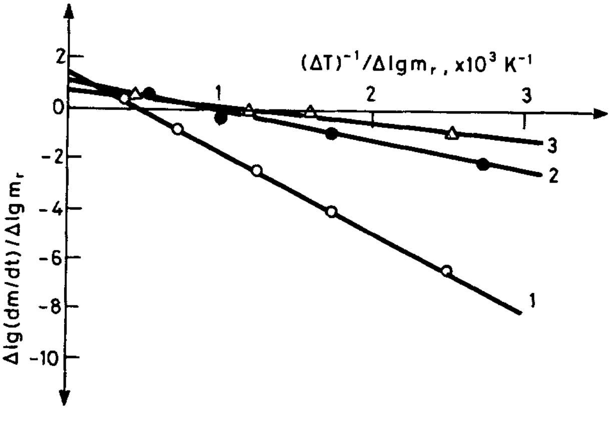

Fig. 2 Kinetics of decomposition of hexamminechromium(III) chloride. 1 - process (1); 2 - process (2); 3 - process (3)

respectively as a value for reaction order of 1.05; 0.90 and 0.75. The obtained values of kinetics parameters show that the thermal decomposition processes of hexamminechromium(III) chloride, carried out at higher temperatures, controlled by diffusion resistances.

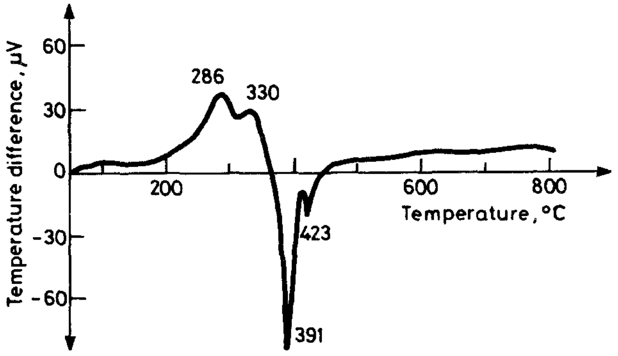

Fig. 3 DSC curve for $[Cr(NH_3)_6]Cl_3$ in air atmosphere at the hetating rate of 10°/min

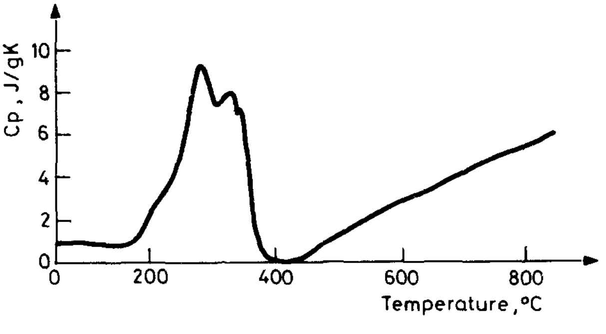

Fig. 4 Dependence $C_p = f(T)$ for solid products reactions of hexamminechromium(III) chloride thermal decomposition

DSC curve for $[Cr(NH_3)_6]Cl_3$, obtained at heating rate of 10° deg/min in air atmosphere, is shown in Fig. 3. The enthalpies for processes, defined on the basis of simultaneous DTA-TG-DTG analysis results, were determined by separate softver, and the obtained results are shown in Table 1.

Table 1 Values for enthalpies of the thermal decomposition process of $[Cr(NH_3)_6]Cl_3$

Processes	Enthalpy, J/g	Limit, °C	Limit, min
1	122	246.2-305.2	22.1-24.9
2	69.2	304.6-355.7	24.8-27.2
3	-391	374.5-449.6	28.1-31.7

Table 2 Numerical values for specific heat capacity (C_p) of solid residues in the course of thermal decomposition processes of $[Cr(NH_3)_6]Cl_3$

Temp., °C	C_p, J/g.K	Temp., °C	C_p, J/g.K	Temp., °C	C_p, J/g.K
60	0.905	310	7.166	560	2.285
70	1.112	320	7.813	570	2.427
80	1.540	330	8.363	580	2.577
90	3.084	340	8.067	590	2.717
100	1.522	350	6.514	600	2.871
110	1.040	360	3.485	610	3.024
120	0.879	370	0.300	620	3.176
130	0.805	380	0.000	630	3.305
140	0.736	390	0.000	640	3.461
150	0.691	400	0.000	650	3.617
160	0.662	410	0.000	660	3.733
170	0.725	420	0.000	670	3.905
180	0.892	430	0.000	680	4.048
190	1.206	440	0.000	690	4.203
200	1.730	450	0.429	700	4.360
210	2.442	460	0.619	710	4.516
220	3.130	470	0.854	720	4.639
230	3.502	480	1.008	730	4.785
240	4.044	490	1.157	740	4.838
250	4.924	500	1.345	750	4.961
260	6.301	510	1.511	760	5.099
270	7.994	520	1.719	770	5.205
280	9.796	530	1.879	780	5.302
290	9.848	540	2.035	790	5.367
300	7.397	550	2.155	800	5.522

C_p (specific thermal capacity) determination of solid product reaction, developed during thermal decomposition process of hexamminechromium(III) chloride, was carried out by parallel method in relation to the sapphire and empty tigel on NETZSCH DSC-404 by appropriate softver [8], and the obtained results are shown in Fig. 4. Numerical values for C_p for each 10° are shown in Table 2.

The obtained DSC results shown that the endothermal feature of decomposition NH_3 process is in good agreement with defined process mechanism, until the exothermal oxidation process of $CrCl_3$ is developed in two stages what is clear seen from the forms of DTA, DTG and DSC curves.

References

1 D. Dollimore, Complex Salts in book Differential Thermal Analysis (Ed. R. C. Mackenzie), Academic Press, London (1970) pp. 427.
2 W. W. Wendlant, C. Y. Chou, J. Inorg. Nucl. Chem., 26 (1964) 943.
3 T. D. George, W. W. Wendlant, J. Inorg. Nucl. Chem., 25 (1963) 395.
4 M. Grotowska, W. Wojciechowski, Mat. Sci., 12 (1986) 9.
5 M. Grotowska, W. Wojciechowski, Bull. Acad. Polon. Sci., Ser. Chim., 27 (1979) 59.
6 M. Grotowska, W. Wojciechowski, ibid, 27 (1979) 69.
7 E. S. Freeman, B. Carroll, J. Physic Chem., 62 (1958) 394.
8 E. Kaisersberger, J. Janoschek, E. Wassmer, Thermochim. Acta, 148 (1989) 499.

Zusammenfassung — Es werden die Ergebnisse einer vergleichenden Thermoanalyse TG-DTG-DTA-DSC des thermischen Zersetzungsprozesses von $[Cr(NH_3)_6]Cl_3$ in Luft dargelegt. Weiterhin wurde die Kinetik und der Mechanismus dieses komplexen thermischen Zersetzungsprozesses, die Enthalpie des Vorganges sowie die temperaturbedingten Änderung der Wärmekapazität dieser Festkörperreaktion bestimmt.